Parameterizing Dynamic Field Simulations from Image Analysis

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The goal of predicting the dynamic and equilibrium phase behavior of complex materials has driven much of the research in condensed matter physics for the past century. The importance of phase transitions in phenomena as diverse as superfluidity, magnetization, blend miscibility, and the creation of rich morphologies observed in block copolymers motivates these intense efforts. Broadly speaking, statistical mechanics models describing phase behavior can be classified as either "field" or "particle" descriptions. The former consists of defining the system's free energy in terms of lattice or continuum fields representing composite quantities such as local magnetic spin or chemical composition. These models are interrogated with analytical and numerical techniques to extract the universal characteristics of different classes of materials. In principle, explicit chemical details can also be included in these field-theoretical models. However, in practice the complexity required to capture the microscopic information and the mathematical stipulations attached to building these models necessitate that the chemistry be embodied in only a few parameters. Specifying those parameters for a real material often requires retreat to empiricism.

Particle-based simulation techniques such as molecular dynamics (MD) or Monte Carlo (MC), on the other hand, rely upon "force-field" models that are thoroughly parameterized to represent specific chemistries. The increasing sophistication of these methods provides the ability to predict the physical behavior of real materials with a high degree of fidelity. Unfortunately, the computational expense that accompanies explicit particle descriptions severely limits the size and time scales accessible relative to those attained with field theoretical models, especially in the case of polymers.

Circumventing the limitations of both methods by mapping from particle-based to field-based representations would not only provide new insight into the relationship between molecular structure and the free energy, but would also revolutionize our capability to model real chemistries and intelligently design new materials. Thus motivated, many investigators are pursuing research to stitch together the patchwork of particle and continuum descriptions into a cohesive framework. Linking a prominent field-based description, the Ginzburg-Landau [1] free energy functional, to explicit particle models would constitute a major advance in these efforts since it serves as a cornerstone for many numerical and analytical theories.

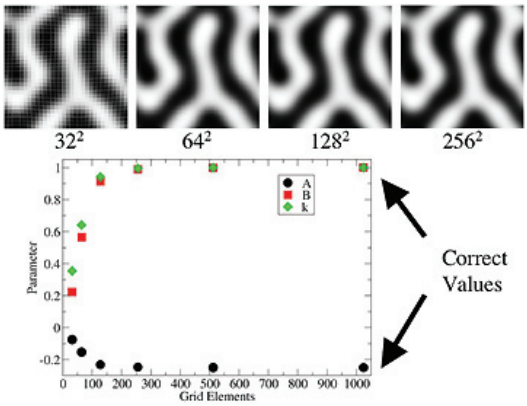
Moreover, the rise of sophisticated experimental techniques that capture actual images of phase separated materials at the nanometer length scale offers new avenues for exploring the relationship between specific chemistries and field-theoretical descriptions. Methods such as atomic force and transmission electron microscopy have taught us much about equilibrium phase separated morphologies and about the accuracy of our theoretical tools, like self-consistent mean field theory. Now, we are poised to extract dynamic information from these characterization tools to parameterize and refine dynamic field theoretical methods.

We are developing an analysis toolset that permits the parameterization of the Ginzburg-Landau free energy functional from a time series of sufficiently resolved images of phase separation obtained from either experiment or simulation. From these images, an estimate of the local composition and the local time derivatives of the composition can be extracted. Given this information, we numerically fit the evolution of the field to the equation of motion derived from the free energy functional and the continuity equation, commonly referred to as the "time-dependent Ginzburg-Landau" equation (TDGL). We therefore denote our analysis tool as the "inverse time-dependent Ginzburg-Landau" method, or iTDGL.

Here, we demonstrate the iTDGL method by applying it to two different sets of simulated two-dimensional images. First, we modeled phase separation in a binary blend by simply choosing a parameterization for the Ginzburg-Landau free energy functional and propagating the TDGL equation of motion forward in time. Hence, we know what solution we should obtain upon applying the iTDGL method because those parameters

were the input for the TDGL simulations. Next, we performed a set of MC simulations on a simple lattice model of a binary blend of polymers below the critical miscibility temperature. Here, we do not know what the correct solutions for the parameters are, but we show below that the results are in excellent agreement with mean field predictions. In both types of simulations, we followed the phase separation dynamics from an initially homogenous mixture.

The TDGL simulations were performed on a 1024^2 grid with a three-parameter free energy functional $f = A\Psi^2+B\Psi^4+k|\nabla\Psi|^2$, where Ψ is the local composition order parameter. The parameters, denoted *A*, *B*, and *k*, capture the extent of chemical mismatch between the two species in the blend and the interfacial penalty associated with having a region rich in one species in close contact with one rich in the other. With the images in hand, we could investigate the affect of image resolution on the accuracy of the iTDGL method by locally averaging over field elements. Figure 1 shows the fitted values of the parameters as a function of the number of grids used per box-side



to represent the data. The data points at 1024 exactly match the parameters chosen in the TDGL simulations, thus validating the iTDGL method. In principle, the values of the parameters are dependent upon the length scale chosen to resolve the field. However, as seen in Fig. 1, the values are stable across a number of coarsening steps so long as the interfacial regions between the phases are well resolved.

We employed the original particle model for polymer phase separation due to Baumgärtner and Heermann [2] for the polymer simulations. The simulations are of a symmetric binary blend of two polymer species at 95% density on a 336^2 lattice. The composition fields were estimated by calculating the local concentrations of a given polymer type in an area defined by 16 lattice elements. Various quantities whose scaling behaviors can be theoretically predicted can be estimated from the iTDGL fit. Figure 2 contains a plot of one such quantity, the correlation length ζ, as estimated from two of the fitted parameters, as a function of the quench depth below the critical temperature T_c. As expected from mean field theory, we observe the correlation length to diverge as the temperature approaches its critical value with the inverse square root of the quench depth.

In summary, we have developed a method to parameterize the Ginzburg-Landau free energy functional from a series of images of the evolution of a phase separating material. Though illustrated here with images produced from computer simulations, the data could just as easily be obtained from experimental methods. We are currently pursuing this possibility with outside collaborators at North Carolina State University.

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[1] P.M. Chaikin and T.C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, England, 1995).
[2] A. Baumgärtner and D.W. Heermann, *Polymer* **27**, 1777 (1986).

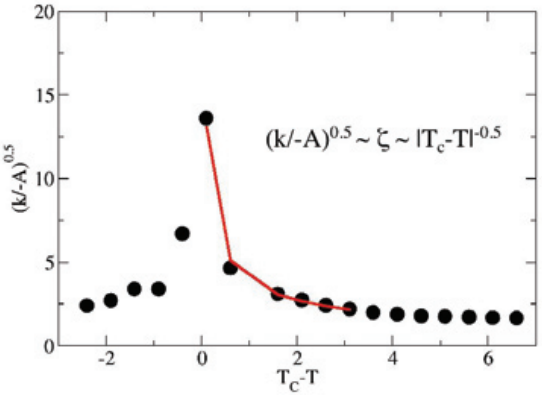

Fig. 1.
The top images show the same field obtained from the TDGL simulation at a given instant in time, but coarsened to different resolutions. The plot represents the iTDGL fit for the three parameters as a function of this coarsening.

Fig. 2.
The circles represent the estimate of the correlation length ζ from the parameters obtained from the iTDGL method. The red line is the best fit to the data close to the critical point T_c.